

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
18 December 2003 (18.12.2003)

PCT

(10) International Publication Number
WO 03/104504 A1

(51) International Patent Classification⁷: **C22B 15/00**

(21) International Application Number: PCT/FI03/00432

(22) International Filing Date: 2 June 2003 (02.06.2003)

(25) Filing Language: Finnish

(26) Publication Language: English

(30) Priority Data:
20021114 11 June 2002 (11.06.2002) FI

(71) Applicant (*for all designated States except US*): **OUTOKUMPU OYJ** [FI/FI]; Riihitontuntie 7, FIN-02200 Espoo (FI).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **HANNIALA, Pekka** [FI/FI]; Runkotie 1 D, FIN-02730 Espoo (FI). **KOJO, Ilkka** [FI/FI]; Kaksosmäki 11 C 9, FIN-02400 Kirkkonummi (FI).

(74) Agent: **OUTOKUMPU OYJ**; Intellectual Property Management, P.O. Box 27, FIN-02201 Espoo (FI).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for all designations*
- *of inventorship (Rule 4.17(iv)) for US only*

Published:

- *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD FOR PRODUCING BLISTER COPPER

(57) Abstract: The invention relates to a method for producing blister copper, according to which method copper concentrate (5), flux (6) and oxygen-enriched air (7) are fed together into a suspension smelting furnace (1), such as a flash smelting furnace, so that there are created at least two molten phases, such as a white metal phase (11) and a slag phase (10); and that the white metal is oxidized after the suspension smelting furnace in at least one oxidizing reactor (12).



WO 03/104504 A1

METHOD FOR PRODUCING BLISTER COPPER

The invention relates to a method defined in claim 1 for producing blister copper.

5

In the flash smelting of copper, dried copper concentrate is fed into a flash smelting furnace together with oxygen-enriched air and silica sand. The energy required in the smelting process is obtained in the oxidation of sulfur and iron. The heat balance of the process is adjusted by means of an oxygen enrichment
10 of the process air, but sometimes oil or natural gas burners are also employed as sources for additional energy. Sulfur is oxidized into sulfur dioxide and iron is oxidized and slagged into iron silicate. The molten phases are separated from the gas in the settler as the slag and matte are settled on the furnace bottom, so that the matte layer is placed lowest underneath. In flash smelting, like in
15 other copper smelting processes, the primary function of slag is to collect in a fluid form that can be tapped all iron oxides and silicatic and oxidic ingredients of the gangue created in the smelting process. Generally slag is cooled, crushed and flotated in order to recover the copper, or it is treated in reducing electric furnace processes. In the matte phase, which generally is further
20 treated in converting, there is obtained 50 – 70 percentages of copper. In the most generally applied Peirce-Smith converting, the iron contained by the matte phase is oxidized when blasting oxygen in the melt and forms, together with the added silica sand, fajalite slag that in the initial step of the converting process floats in the reactor on the surface of the white metal that is rich in copper. The
25 white metal contains 70 – 80 percentages of copper. When further blasting oxygen into the white metal, there is created blister copper, the copper content whereof is of the order 99 percentages. The slag still contains 5 – 10 percentages of copper, which is recovered by flotation and by feeding the slag concentrate that is rich in copper back into the flash smelting furnace or by
30 treating the slag in reducing conditions for example in an electric furnace.

In principle it is economically sensible to directly produce blister copper, i.e. blister copper from sulfidic concentrate in one process step in a suspension reactor, with due respect to certain restrictions. The biggest problem here is that in said process, there is created a lot of slag, and also a large amount of
5 copper is collected in this slag. On the other hand, the treatment of slag in order to recover the copper contained therein causes extra expenses for the process. When the copper content in the concentrate is sufficiently high, typically at least 37 percentages by weight, it is economically profitable to produce blister copper in one process step. If the concentrate contains only slight amounts of iron or
10 other slag-forming components, in which case the amount of created slag is not so high, also the processing of a concentrate with a lower copper content is profitable. When producing blister copper, there is generally needed a two-step slag cleaning for the created slag in order to obtain a sufficiently high yield for the recovered copper.

15

According to the prior art, when operating within a given oxygen potential area, there appears so-called white metal in copper smelting, and in that case the copper content of the respective slag phase is essentially lower than in a case where the blister copper is in balance with the slag phase. In figure 1 (INSKO
20 261608 VIII, page 9), there is illustrated a sulfur-oxygen potential diagram for a Cu-Fe-S-O-SiO₂ system at the temperature 1300° C. In the figure there are seen contents of various phases occurring in the copper smelting process in different conditions. From the figure it can be seen that when white metal is present, the copper content of the respective slag is lower than with a slag
25 where the blister copper is in balance.

From the publication PCT 00/09772, there is known a process for smelting copper concentrate in the presence of oxygen by continuously oxidizing the concentrate or the matte at a temperature of 1300 degrees or lower. According
30 to the process, the copper sulfide concentrate is smelted, the majority of the contained iron is removed as slag, and the majority of the sulfur turns into sulfur dioxide. The obtained product is white metal, matte or blister copper.

The object of the present invention is to eliminate some of the drawbacks of the prior art. Another object of the invention is to prevent the creation of a slag with a high copper content in the production of blister copper.

5

The invention is characterized by what is set forth in the preamble of claim 1. Other embodiments of the invention are characterized by what is set forth in the other claims.

The method according to the invention for producing blister copper has several
10 advantages. According to the method, concentrate, flux and oxygen-enriched air are together fed into a suspension smelting furnace, such as a flash smelting furnace, so that there are created at least two molten phases, a white metal phase and a slag phase, and the white metal is oxidized after the suspension smelting furnace at least in one oxidizing reactor. According to the
15 method, the operations in the suspension smelting furnace are advantageously carried out in conditions that provide for the creation of white metal, which means that the oxygen potential in the furnace is within the range 10^{-7} - 10^{-6} and the sulfur dioxide partial pressure is within the range 0,2-1. White metal is essentially composed of copper (70 – 80%) and sulfur. The white metal created
20 in the smelting does not substantially contain any slagging components. When operating in the above described conditions, there is advantageously created low-copper slag that is suited to be directly treated for recovering the copper, and there is not needed any separate primary reduction of slag for instance in an electric furnace.

25

The white metal is tapped out of the furnace either in continuous operation or in batches, in order to be oxidized in an oxidizing reactor, where the sulfur contained in the white metal is oxidized by using oxygen-enriched air, so that there are created sulfur dioxide and blister copper, but hardly any slag.
30 According to a preferred embodiment of the invention, the oxidizing reactor is arranged in a stationary fashion in connection with the suspension smelting furnace. According to another preferred embodiment of the invention, the

oxidizing reactor is connected to the suspension smelting furnace by a closed melt launder that provides for the transferring of the melt. When the oxidizing reactor is a closed reactor, the collection and recovery of the gases created in the process is more advantageously controlled. According to a preferred
5 embodiment of the invention, the oxidizing reactor is preferably a surface blasting reactor. According to another preferred embodiment, the oxidizing reactor is an injection reactor, by which also white metal in a solid state can advantageously be melted by injecting it into the melt together with oxidizing gas. The employed oxidizing reactor is advantageously for example of the type
10 Ausmelt, Isasmelt or Mitsubishi.

Slag is tapped separately from the suspension smelting furnace and treated, according to a preferred embodiment of the invention, in an electric furnace in order to recover the copper content thereof. According to another preferred
15 embodiment of the invention, slag is after the suspension smelting furnace treated in flotation in order to recover the copper content. When applying the method according to the invention, there is advantageously not created any slag with a high copper content, and the unnecessary recirculation of copper and resulting copper losses are avoided.

20

The invention is explained in more detail below, with reference to the appended drawings.

Figure 1 A sulfur-oxygen potential diagram for a Cu-Fe-S-O-SiO₂ system at the temperature of 1300° C

25 Figure 2a A process diagram of the process according to the invention.

Figure 2b A process diagram of a process according to another preferred embodiment of the invention.

Figure 2a illustrates the method according to the invention. Now concentrate 5,
30 flux 6 and oxygen-enriched air 7 are together fed into a flash smelting furnace

1, so that at the lower part 4 thereof there are created two molten phases, a white metal phase 11 and a slag phase 10. White metal 11 is oxidized after the flash smelting furnace in one oxidizing reactor 12, and there is created blister copper 15. In addition to white metal and slag, in the flash smelting furnace there is created a small amount of blister copper, which also is conducted into the oxidizing reactor in 12. The process gases created in the flash smelting furnace 1 are conducted via the furnace uptake shaft 2 to a waste heat boiler 8, where the created dusts 9 are recirculated back into the flash smelting furnace, and the gases 17 are conducted to further treatment. The white metal 11 is tapped out of the furnace 1 either in continuous operation or in batches into the oxidizing reactor 12, where the sulfur contained in the white metal is oxidized by oxygen-enriched air 16, so that there are created sulfur dioxide and blister copper 15, but not slag. According to a preferred embodiment of the invention illustrated in figure 2a, the oxidizing reactor 12 is arranged to be installed in connection with the flash smelting furnace in a stationary fashion. In another embodiment of the invention, illustrated in figure 2b, the oxidizing reactor 12 is connected by means of a melt launder 13 directly to the flash smelting furnace. The slag 10 created in the flash smelting furnace 1 is conducted into slag treatment 14, alternatively either into an electric furnace or into flotation in order to recover the copper content of the slag. According to a preferred embodiment of the invention, the oxidizing reactor is preferably a surface blasting or injection reactor, in which case also solid white metal can advantageously be melted by injecting it into the melt together with the oxidizing gas. The oxidizing reactor is preferably for example of the type Ausmelt, Isasmelt or Mitsubishi.

25

The invention is illustrated below by the following example.

EXAMPLE

By applying the method according to the invention, copper concentrate with a content of 30% Cu, 28% Fe, 30% S, 6% SiO₂ is smelted in a flash smelting furnace at the rate of 163 tph (tph = tons/hour) together with silica sand, which is fed into the furnace at 21 tph.

30

During the smelting process, into the flash smelting furnace there is blown air at the rate of 63,493 Nm³/h and oxygen at the rate of 21956 Nm³/h, so that the oxygen enrichment is 41 % and the oxygen coefficient is 171 Nm³ O₂ when
5 calculated per one whole ton fed in.

As a result of the oxidizing reactions, in the flash smelting furnace there is created molten white metal at 62,004 kg/h (content 79% Cu, 0.5% Fe) and slag at 109,702 kg/h (content 4% Cu, 44% Fe). In addition, there is created a small
10 amount of dust that is recirculated back into the smelting furnace.

The slag is treated in a slag enrichment plant, so that the rate of created slag is 8,844 kg/h (content 46% Cu, 25% Fe), and said slag is then fed back into the flash smelting furnace together with the concentrate.

15

The created white metal is treated in an oxidizing reactor, into which there is fed technical oxygen at 4,328 Nm³/h and air at 18,979 Nm³/h. Now there is created blister copper at 49,274 kg/h (content 98% Cu, 0.04% Fe) and a small amount of slag (1 ton/h, content 50% Cu, 27% Fe). The slag is granulated and fed back
20 into the flash smelting furnace.

In the example given above, the total quantity of copper recirculated back into the flash smelting furnace in slag concentrate and in the slag from the oxidizing reactor is 4,575 kg Cu, which corresponds to about 9% of the whole copper
25 quantity contained in the concentrate. If the concentrate were smelted directly into blister, the slag quantity would be about 130 t/h, and it would contain even more than 50% of the total copper quantity contained in the concentrate.

For a man skilled in the art, it is obvious that the various embodiments of the invention are not restricted to the examples illustrated above, but may vary
30 within the appended claims.

CLAIMS

1. A method for producing blister copper, according to which method copper concentrate (5), flux (6) and oxygen-enriched air (7) are fed together into a suspension smelting furnace (1), such as a flash smelting furnace, so that there are created at least two molten phases, such as white metal (11) and slag (10), **characterized** in that white metal is oxidized after the suspension smelting furnace in at least one oxidizing reactor (12).
2. A method according to claim 1, **characterized** in that oxidizing reactor (12) is arranged to be installed in connection with the suspension smelting furnace (1) in a stationary fashion.
3. A method according to claim 1, **characterized** in that the oxidizing reactor (12) is connected to the suspension smelting furnace (1) by a melt launder (13).
4. A method according to claim 1 – 3, **characterized** in that the oxidizing reactor (12) is a surface blasting reactor.
5. A method according to claim 1 – 3, **characterized** in that the oxidizing reactor (12) is an injection reactor.
6. A method according to claim 5, **characterized** in that into the oxidizing reactor (12), there also is injected solid white metal.
7. A method according to claim 1, **characterized** in that the slag (10) is after the suspension smelting furnace (1) treated in an electric furnace in order to recover the copper content thereof.

8. A method according to claim 1, **characterized** in that the slag (10) is after the suspension smelting furnace (1) treated in flotation in order to recover the copper content thereof.

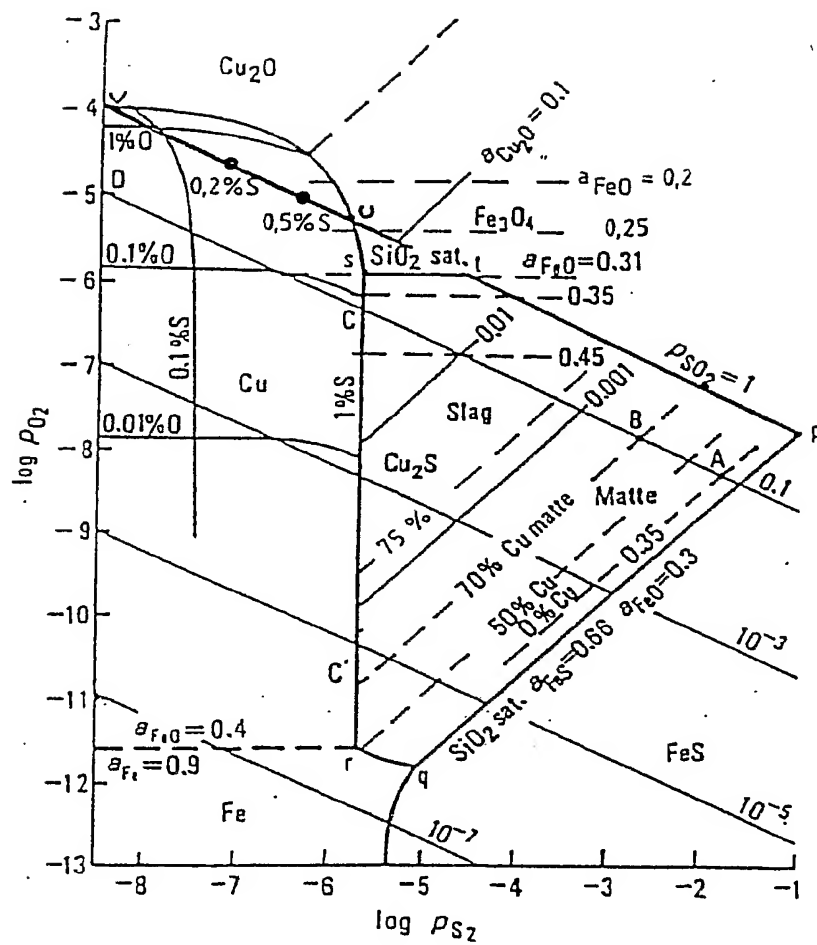
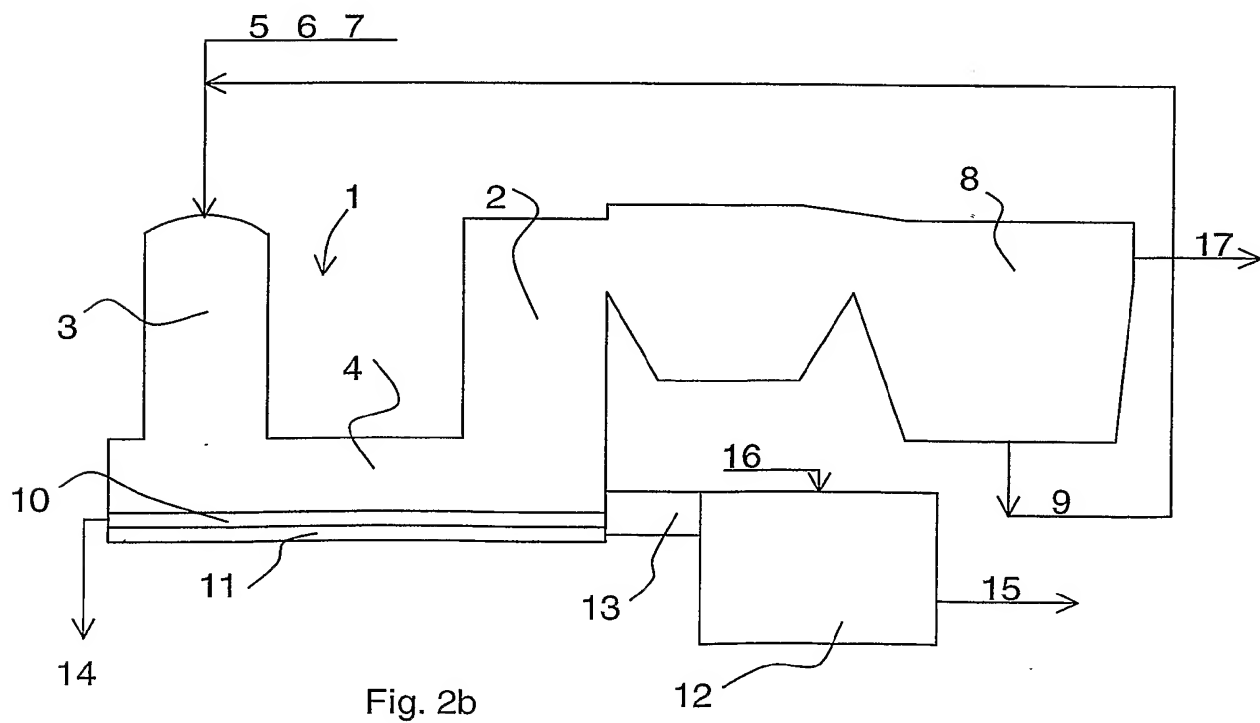
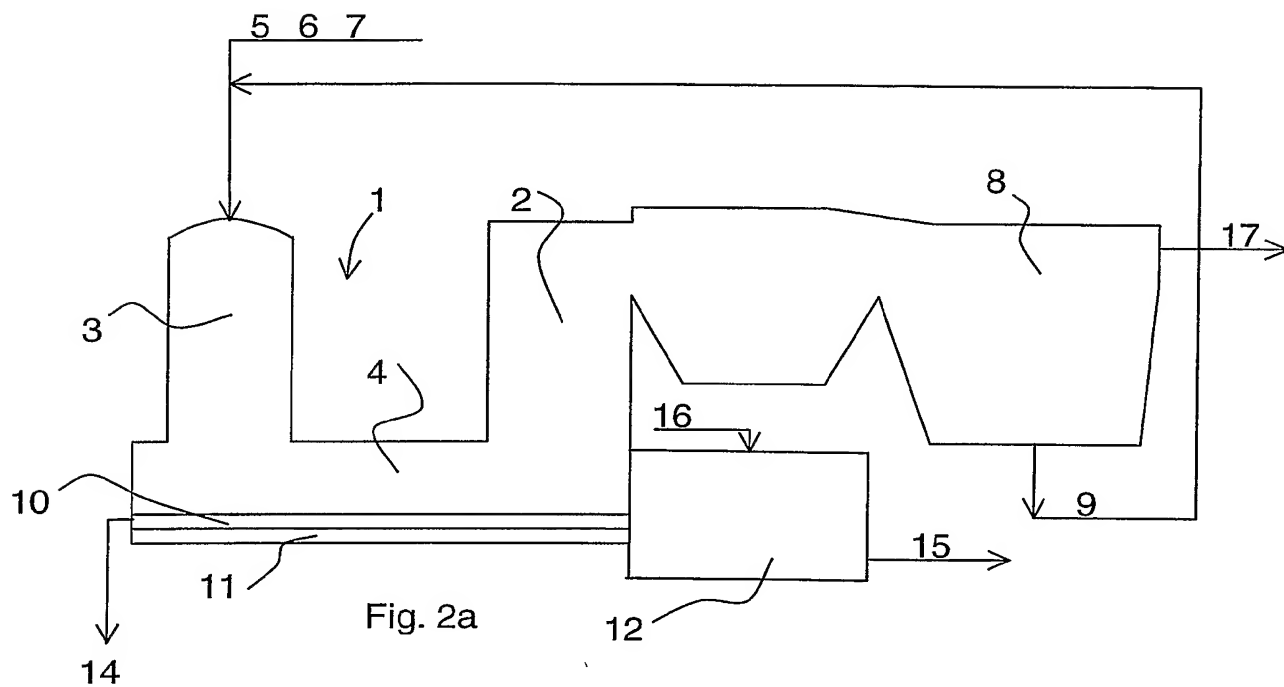


Fig. 1.

2/2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 03/00432

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C22B 15/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4470845 A (JOHN C. YANNOPOULOS), 11 Sept 1984 (11.09.84), column 4, line 37 - line 52 --	1-8
X	US 4416690 A (KENNETH J. RICHARDS ET AL), 22 November 1983 (22.11.83), figure 1, abstract --	1-8
X	US 4349383 A (KIRANENDU B. CHAUDHURI), 14 Sept 1982 (14.09.82), claim 1, abstract --	1-8

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

8 Sept 2003

Date of mailing of the international search report

09-09-2003

Name and mailing address of the ISA/

Swedish Patent Office

Box 5055, S-102 42 STOCKHOLM

Facsimile No. +46 8 666 02 86

Authorized officer

Linda Melin/MP

Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 03/00432

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4528033 A (BENGT T. ANDERSSON), 9 July 1985 (09.07.85), column 2, line 9 - line 26; column 2, line 49 - line 55, Example --	1-8
X	US 5194213 A (CARLOS M. DIAZ ET AL), 16 March 1993 (16.03.93), column 2, line 28 - line 52 --	1-8
X	US 3980470 A (HIROSHI KAMETANI ET AL), 14 Sept 1976 (14.09.76), column 1, line 51 - line 65; column 2, line 30 - line 37 --	1-8
A	US 4030915 A (OLAVI AUGUST AALTONEN ET AL), 21 June 1977 (21.06.77), page 4, column 64 - page 5, column 4, abstract, Table 1 -- -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

26/07/03

International application No.

PCT/FI 03/00432

Patent document cited in search report			Publication date	Patent family member(s)		Publication date
US	4470845	A	11/09/84	CA	1220631 A	21/04/87
				JP	59166637 A	20/09/84
				ZA	8400094 A	28/11/84

US	4416690	A	22/11/83	AU	545117 B	27/06/85
				AU	8431682 A	09/12/82
				BE	893371 A	01/10/82
				BR	8203192 A	17/05/83
				CA	1195125 A	15/10/85
				DE	3220609 A,C	27/01/83
				FI	73742 B,C	31/07/87
				FI	821899 D	00/00/00
				FR	2506786 A,B	03/12/82
				GB	2099457 A,B	08/12/82
				IN	157891 A	19/07/86
				JP	1744129 C	25/03/93
				JP	2001216 B	10/01/90
				JP	58006946 A	14/01/83
				MX	159378 A	22/05/89
				PH	15554 A	11/02/83
				PL	141491 B	31/07/87
				PL	236690 A	31/01/83
				SE	460974 B,C	11/12/89
				SE	8203064 A	02/12/82
				YU	44208 B	30/04/90
				YU	115582 A	20/03/85
				ZA	8203316 A	29/06/83
				ZM	3882 A	21/01/83

US	4349383	A	14/09/82	CA	1159261 A	27/12/83
				DE	2941225 A	23/04/81
				ZM	8780 A	21/10/81

US	4528033	A	09/07/85	CA	1225527 A	18/08/87
				FI	67727 B,C	31/01/85
				FI	832170 A	16/12/84

US	5194213	A	16/03/93	AU	2059492 A	04/02/93
				CA	2074678 A,C	30/01/93
				DE	4225010 A	04/02/93
				FI	103991 B	00/00/00
				FI	923401 A	30/01/93
				GB	2258246 A,B	03/02/93
				GB	9215732 D	00/00/00
				JP	5214460 A	24/08/93
				KR	212947 B	02/08/99
				MX	9204392 A	31/05/94
				ZA	9205650 A	28/04/93

US	3980470	A	14/09/76	CA	1051205 A	27/03/79
				JP	899418 C	25/02/78
				JP	50128671 A	09/10/75
				JP	52030259 B	06/08/77

INTERNATIONAL SEARCH REPORT

Information on patent family members

26/07/03

International application No.

PCT/FI 03/00432

Patent document cited in search report			Publication date	Patent family member(s)		Publication date
US	4030915	A	21/06/77	AU	497653 B	21/12/78
				AU	8405275 A	24/02/77
				CA	1057061 A	26/06/79
				DE	2536392 A,B	20/05/76
				FI	52358 B,C	02/05/77
				FI	326674 A	12/05/76
				PL	95510 B	31/10/77
<hr/>						